

Effect of Reaction Time and Acids in Chemical Leaching of Heavy Metals in Sewage Sludge

Luke N. Ukiwe* • Chinonye I. Iwu

Department of Chemistry, Federal University of Technology, P.M.B 1526, Owerri, Nigeria

Corresponding author: * luggil2002@yahoo.com

ABSTRACT

The present study indicates the concentration (mg/l) of heavy metals (HMs) following solubilization with nitric and acetic acids at various contact times. The concentration of HMs was found to be highest when solubilization was performed at a contact time of 1 hr using both acids except for Mn in both acids and Cu in nitric acid. There was no trend in HMs extraction as contact time increased. Solubilization at 6 hrs extracted much less HMs using both acids. Cu (3.3416 mg/l) was the overall highest metal extracted using acetic acid, while Cd (0.0012 mg/l) was the overall lowest metal extracted using acetic acid at 1 hr contact time.

Keywords: acetic acid, contact time, contamination, extraction, solubilization, wastewaters

INTRODUCTION

Maximum heavy metal (HM) solubilization has been achieved when the appropriate conditions of acids and contact time are applied. Sludge samples are found to contain significant amounts of HMs (Cr, Cu, Ni, Pb and Zn) especially when the sludge is subjected to acid treatment using hydrochloric, sulphuric, nitric or phosphoric acids. In a study to investigate the removal of HMs from sewage sludge (SS) by acid treatment, Naoum *et al.* (2001) noted that the optimum combination in terms of metal removal efficiency was sought by applying a ratio of 1: 5 of sludge quantity per volume of acid at a contact time of 60 min. Ukiwe and Oguzie (2008), in their study on the effect of pH and acids on HMs solubilization of domestic SS demonstrated that by using about 10 ml of a 50% (v/v) sulphuric acid solution at a contact time of 30 min, about 1095.9538 mg/l of selenium was extracted at pH 4.0, while 0.2002 mg/l of Ni was the least HM extracted using the same acid and pH conditions.

The uptake of ions by plants is a phytoremediation process for the extraction of HM from aquatic systems. Water hyacinth (*Eichhornia crassipes*) is a free-floating tropical aquatic plant that grows rapidly at temperatures ranging from 28 to 30°C and at pH 4.0-8.0. The rapid growth rate of the plant on such water bodies has created an environmental impact that has attracted much attention to the plant. It is suggested that the phytoextraction process is enhanced when metal solubilization is performed at a contact time of 2 hrs (Ukiwe *et al.* 2008a). Another study conducted by Ukiwe and Ogukwe (2007) on the potassium ion uptake by water hyacinth on the Lower reaches of the Niger River, Nigeria indicated that maximum extraction efficiency is obtained when solubilization of the plant is carried out with *aqua regia* (1: 3 of nitric and hydrochloric acid) at a contact time of 2 hrs. It is generally believed that the preparation and performance of activated carbon is governed by the ash content (Ukiwe *et al.* 2008b). Ash is the substance that remains after any material has been burnt. The amount of minerals in certain substances can be determined by analyzing the ash left when they are burnt. Ash is composed chiefly of earthy mineral particles. Aquatic and terrestrial plants contain some amount of trace elements. By ashing

samples of water hyacinth, *Gmelina arborea*, and *Chlorophora excelsa*, Ukiwe *et al.* (2008b) demonstrated that a heating time of 2 hrs in a muffle furnace produce ash when digested with *aqua regia* at a contact time of 10 min produce 71, 83 and 82% copper for water hyacinth, *Gmelina arborea*, and *Chlorophora excelsa*, respectively. Pot and leaching column experiments have been conducted to optimize chelator-assisted phytoextraction of Pb from contaminated soils. Results revealed that optimum phytoextraction occurred when 5 mM ethylene diamine tetracetic acid (EDTA) was added in a single dose for a contact time of 10 days in low Pb soil, while for high Pb soils, five intermittent doses of 10 mM EDTA were applied at a reaction time of 7 days (Liu *et al.* 2008). Combined with column experiments, it was inferred that chelator-assisted phytoextraction was more suitable for the removal of HMs from slightly contaminated soils.

HMs should be removed in soil systems for the safety of the environment, and to rehabilitate polluted sites. Chelating agents such as EDTA have been applied in different situations in phytoremediation to enhance the extraction of HMs by plants to assess the availability of HMs in soil injected with biosolids and in composted biosolids with amendment (Liphadzi and Kirkham 2006). Five EDTA doses were applied into either soil injected with biosolids (soil) or composted biosolids (compost) in flasks. The soil and EDTA solution in flasks were shaken for a reaction period of 4 hrs. The flasks were allowed to stand for another 2 hrs contact time and then decanted and the resultant mixture filtered and tested for HMs concentration. It was shown that the soil which received EDTA had a higher concentration of HMs than that injected with biosolids. Essential HMs (Cu, Fe, Mn, and Zn) increased in the organs of hybrid poplar (*Populus deltoids*) plants grown in the composted biosolids where EDTA at 2.0 g kg⁻¹ soil was applied. The concentration of HM in the plant organs were not affected by EDTA in soil injected with biosolids (Liphadzi and Kirkham 2006).

Chemical or biological acidification of sewage sludge elutes HMs from the sludge and the elution efficiencies of HMs depend on the pH and contact reaction time. A study conducted on the removal of HMs without P loss from anaerobically digested SS by batch experiments using hydro-

gen peroxide (H_2O_2) and/or iron sulphate under acidified conditions of 24 hrs reaction time at pH 3.0, and a combined process of 0.1% H_2O_2 and 1 g Fe L^{-1} ferric sulphate showed that enhanced initial elution rate of Cu and Cr was obtained in a combined process compared to the addition of either ferric sulphate or H_2O_2 indicating that oxidants stronger than H_2O_2 were produced in the sludge. The research concluded that there is a possibility that the combined process could remove HMs effectively without P loss from anaerobically digested SS (Ito *et al.* 2008). Activated sludge systems for wastewater treatment produce large amounts of sludge. Normally, this sludge is stabilized by anaerobic digestion and afterwards it is dewatered and disposed in landfills. Marchioretto *et al.* (2002) proposed sulphide and hydrogen precipitation followed by filtration could be used for HM removal from anaerobically digested sludge. Before submitting to precipitation, the sludge was aerated and acidified until the pH value was equal to 1 in order to attain the best conditions for HM solubilization. However, to evaluate the distribution of HMs in the solid and liquid parts of the sludge, the sludge was centrifuged at 4000 rpm for a contact time of 20 min and the supernatant was then analyzed for trace metals. The result obtained indicated that at 20 min contact time, the combination of hydroxide and sulphide precipitation before physical separation was capable of promoting the efficient removal of HMs from anaerobically digested sludge. The best percentages achieved for HM removal were: Pb (100%), Cr (99.9%), Cu (99.7%), and Zn (99.9%).

Metals that have been deposited in contaminated bottom-sediments could be released to the water column with changes in different hydrobiological and physico-chemical conditions. Mobility and bioavailability of metals in sediments depends also on their chemical forms. It is necessary to determine metal speciation when evaluating the amounts of metals leached into water from the bottom-sediments under changing environmental conditions. Research on aeration of the above-sediment water on the amount of copper released from contaminated bottom sediments has noted that, a contact time of 24 hrs of extractant (1 M KNO_3 , 0.5 M KF, 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$, 0.1 M EDTA, and 6.0 M HNO_3) with the sample in the ratio of 50: 1 of extractant to dry mass of the sediment, leached 60% Cu as the highest metal in the sulphide form from the bottom sediment in the non-aerated systems. Only about 8% Cu was obtained in aerated systems. Aeration, the study noted, caused a considerable decrease in the amounts of metals in sulphide systems irrespective of the contact time (Loska and Wiechuła 2000).

Bioleaching is another technique used to remove HMs from anaerobically digested SS. Bioleaching is the process of extracting HMs from contaminated systems using biological agents such as bacteria. The effects of sulphur concentration, initial pH of sludge, sludge solid content, and contact time on metal bioleaching were examined by Páthak *et al.* (2009) using anaerobically digested SS. Results of analysis showed that using 2 g L^{-1} elemental sulphur, indigenous sulphur oxidizing microorganisms can bring down pH to a value needed for significant metal solubilization at a contact time of 4–6 days to optimize the concentration of elemental sulphur for efficient bioleaching. The effect of using FeS_2 as an energy source on the bioleaching of HMs and nutrients (nitrogen and phosphorus) from anaerobically digested sludge using isolated indigenous iron-oxidizing bacteria was investigated by Wong *et al.* (2004). They reported that addition of FeS_2 in the range of 0.5 – 4.0 g L^{-1} accelerated the acidification of sludge and raise the oxidation-reduction potential of the sludge medium with an inoculation of 15% (v/v) of active bacteria, thus resulting in an overall increase in metal dissolution efficiency. After 16 days bioleaching reaction time, at 28°C and an initial pH of 3.0, up to 99% Zn, 65% Cr, 74% Cu, 58% Pb, and 84% Ni were removed from the sludge. Zhou *et al.* (2005) also reported that after 10 days of bleaching, the pH of sludge reached 1.5 and almost 100% of Cr was leached when the

effects of initial sulphuric acid addition on bioleaching process and influences of recycled rate of acidified bioleached sludge on subsequent bioleaching reaction was studied.

The removal of HMs by acidification in different concentrations and temperatures has been a common scheme applied in metal extraction. In addition, the chemical forms of the metals could also be investigated using the sequential extraction procedures. In applying this scheme to evaluate metal availability in sludge, Stylianou *et al.* (2007), showed that at the contact time range from 1–60 minutes, and acid concentration range of 10–20%, and 25–80°C temperature range, the optimum combination of metal extraction was achieved when the sludge samples were in contact with H_2SO_4 (20% v/v) for 30 min at 80°C, since this experimental condition resulted in the highest HMs removal efficiency. Other authors (Abbeh *et al.* 2007; Nwajei and Iwegbue 2007a, 2007b) have suggested various methods of acid solubilization with a contact time of 2 hrs between acid solution and sample at a temperature range between 100–120°C for maximum HMs extraction efficiency.

The objective of the present study was to assess the effect of reaction time and acids (nitric and acetic acids) on the removal efficiency of HMs from domestic SS.

MATERIALS AND METHODS

Sludge samples were collected from the septic tank of the male ward of the Federal Medical Centre, Owerri, Nigeria. A 50 L plastic container previously washed and rinsed with deionised water was used to fetch the sludge sample which was latter taken to the chemistry laboratory and allowed to stand for 24 hrs at 28°C. Samples for the analysis were continually drawn from this 50 L plastic container. A quantity of sample containing 2 L of sewage was measured into a 2-L beaker previously washed and rinsed with deionised water. About 300 ml of sludge sample was measured from the 2-L sample into a 1000-ml beaker and centrifuged (Micro Centrifuge Model 5415C) for 1 hr at 200 rpm at 28°C. The resultant solution was filtered through Whatman No. 42 filter papers. About 10 ml of the sludge filtrate was measured into a 100 ml beaker and 30 ml of a 30% (v/v) nitric acid solution was added and the mixture was stirred thoroughly for 5 min. The pH of the mixture was maintained at 3.0 and heated on a Bunsen burner for 30 min with intermittent addition of deionised water to prevent drying up of the mixture. The mixture was cooled and filtered through Whatman No. 42 filter papers. The resultant filtrate was made up to 100 ml with a 100 ml standard flask and 100 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionised water. This 10 ml filtrate was used for analysis with an Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the metals Cd, Mn, Pb, Ni, and Cu. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described by Ukiwe *et al.* 2008b. The above procedure was repeated for 30% (v/v) nitric acid for a contact time heating period of 1, 2, 4 and 6 hrs. While using 30% (v/v) acetic acid, the entire procedure was repeated for 30 min, 1, 2, 4 and 6 hrs.

Data analysis

Data were reported as arithmetic mean, standard deviation and standard error of the mean. Analysis of variance (ANOVA) was employed to determine difference between mean concentration levels of HM at various acids and reaction times. Moreover, the standard error of the difference between means and the generalized *t*-test were used to observe for significance in HM concentration in acids and reaction times at $P < 0.01$.

RESULTS AND DISCUSSION

Heavy metals occur in the aquatic environment and on land in a number of forms namely; dissolved particulates, complexes and total metal forms. In recent years, much attention has been given to the concentration of toxic HMs in fresh water and aquatic bodies. HMs are discharged into systems from non-point sources such as agricultural and

Table 1 Concentration of heavy metals in sludge samples using nitric acid for solubilization.

Reaction time	30 mins ^(a)		1 hr ^(b)		2 hrs ^(c)		4 hrs ^(d)		6 hrs ^(e)	
	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³
Cd	0.0036 ± 1.0	5.7	0.0061 ± 2.1	0.1	0.0011 ± 1.0	5.7	0.0026 ± 2.3	0.1	0.0051 ± 1.3	7.5
Mn	0.0062 ± 1.1	6.3	0.0596 ± 2.2	0.1	0.0706 ± 0.5	2.8	0.0592 ± 0.2	1.1	0.0376 ± 1.0	5.7
Pb	1.6963 ± 2.2	0.1	2.8983 ± 5.2	0.3	1.7049 ± 5.0	0.2	1.5958 ± 3.6	0.2	1.3162 ± 0.9	5.2
Ni	0.0028 ± 8.2	0.0	0.0077 ± 8.8	0.5	0.0467 ± 2.0	0.1	0.0466 ± 3.2	0.1	0.0012 ± 1.0	5.7
Cu	2.8641 ± 1.1	6.3	2.8685 ± 0.6	3.4	2.8524 ± 1.3	7.5	2.9606 ± 0.2	1.1	2.8124 ± 1.1	6.3

SEM: Standard Error of the Mean; *t*-test between (a)/(b) = 0.31; (b)/(c) = 0.24; (c)/(d) = 0.00; (d)/(e) = 0.11**Table 2** concentration of heavy metals in sludge samples using acetic acid for solubilization.

Reaction time	30 mins ^(a)		1 hr ^(b)		2 hrs ^(c)		4 hrs ^(d)		6 hrs ^(e)	
	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³	Mean (mg/l) ± SD × 10 ⁻²	SEM × 10 ⁻³
Cd	0.0048 ± 2.5	0.1	0.0012 ± 1.0	5.7	0.0021 ± 1.0	5.7	0.0044 ± 1.0	5.7	0.0014 ± 2.1	0.1
Mn	0.0404 ± 1.1	6.3	0.0195 ± 7.9	0.4	0.0216 ± 1.2	6.9	0.0245 ± 1.1	6.3	0.0159 ± 1.5	8.6
Pb	1.6340 ± 0.0	0.0	1.6989 ± 1.3	7.5	1.6006 ± 1.1	6.3	1.4201 ± 2.0	0.1	1.4641 ± 0.9	5.2
Ni	0.0532 ± 3.2	0.1	0.0703 ± 2.9	0.1	0.0357 ± 2.3	0.1	0.0576 ± 4.6	0.2	0.0248 ± 1.1	6.3
Cu	2.9621 ± 1.0	5.7	3.3416 ± 0.9	5.2	3.1523 ± 1.0	5.7	3.3205 ± 2.4	0.1	3.1123 ± 1.3	7.5

SEM: Standard Error of the Mean; *t*-test between (a)/(b) = 0.31; (b)/(c) = 0.24; (c)/(d) = 0.00; (d)/(e) = 0.11

urban run-offs (Okuo and Iyasele 2004).

Tables 1 and **2** present the values of concentration (mg/l) of HMs following solubilization with nitric and acetic acids at various contact times. The concentration of HMs was found to be highest when solubilization was performed at a contact time of 1 hr using both acids except for Mn in both acids and Cu in nitric acid. It was observed that there was no trend in HMs extraction as the contact times was ascended. It was also observed that solubilization at 6 hrs extracted much less HMs using both acids. Cu (3.3416 mg/l) was the overall highest metal extracted using acetic acid, while Cd (0.0012 mg/l) was the overall lowest metal extracted using acetic acid at 1 hr contact time. This fact is in agreement with the study conducted by Yoshizaki and Tomida (2000). They reported that Cu is easily removed from sludge when solubilization is carried out at a contact time of 1 hr.

Standard deviation, standard error of the mean and the generalized *t*-test between mean concentration (mg/l) at various reaction times are given in **Table 1** and **2**. $P < 0.01$ when these values were tested at 8 degrees of freedom between reaction times.

Recent studies appear to suggest that organic acids such as citric and oxalic acids seemed to be more promising as chemical extracting agents for removal of HMs from contaminated sludge at a contact time of 1 hr, since these acids are biodegradable and can attain a higher metal extraction efficiency at mildly acidic pH at this contact time compared to other contact times. Dacera and Babel (2006) concluded that at 2 hrs contact time, Zn removal from sludge solutions at pH 2.33 was 100% although at pH 3.0, using citric acid, the removal ratio of Zn dropped to 80%. Kuo *et al.* (2005) also reported a leaching time as high as 18 hrs for traditional acid extraction of Cu from sludge obtaining about 78% Cu extraction efficiency using nitric acid together with microwave assisted treatment. However, when the microwave powers were increased to 800 watts, and the contact time reduced to 30 min, the extraction efficiency of Cu increased to 93%. The study inferred that microwave assisted treatment reduced the leaching time but improved the leaching efficiency. Coagulants have been used to remove HM in drinking water and effluent. A study conducted using trimethoxysilane demonstrated that due to the large specific surface area of the compound, it provides myriad active points for the adsorption of HMs. When the heavy metal effluent was added to the colloidal solution of silicate at a contact time of 30 minutes, the removal of HMs (Pb and Cr) was up to 99% (Li *et al.* 2004). The study noted that due to drawbacks inherent in other HMs extraction methods such as ion exchange and complexation, adsorption and coagulation methods can offer a positive alternative for high

efficiency extraction.

Toxicants such as HMs and chlorinated hydrocarbons such as pesticides and polychlorinated biphenyls (PCBs) are of concern in all proposals of environmental management. The present study has demonstrated that the removal of HMs from the environment should take into cognizance the type of acids used, pH, and optimum extraction contact time.

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